Stability of Ion Exchange Resin Under Freeze–Thaw or Dry–Wet Environment

Martha Mamo,* Daniel Ginting, Roger Renken, and Bahman Eghball

ABSTRACT

Ion exchange resins have widely been used in mineralization studies of organic materials. However, the stability of resin (anionic and cationic) under changing physical environmental conditions is not well known. Our objective was to evaluate N and P adsorption or desorption characteristics of resins exposed to freeze–thaw or dry–wet cycles. Mixed bed resins (1:1 oven-dry mass strong base anion A464-D and strong acid cation C-249) were subjected to 0, 1, and 30 freeze–thaw or dry–wet cycles. To accomplish the dry–wet cycles, fresh resin was kept in a forced-air oven at 25 (±2)°C for 28 h and rewetted to initial moisture condition for 20 h. To accomplish the freeze–thaw cycle, fresh resin was frozen for 16 h and thawed to room temperature for 8 h daily. At the end of the freeze–thaw or dry–wet cycles, resin was equilibrated with 3.2 m*M* L^{-1} NH_4–N, 3.2 m*M* L^{-1} NO_3–N, or 0.97 m*M* L^{-1} PO_4–P for a period of 1 h. Dry–wet cycles induced desorption of N and P associated with shrinkage of resins and expulsion of interstitial liquid. At the highest dry–wet cycle, 3.3, 0.35, and 0.15% of the total adsorbed PO_4–P, NH_4–N, and NO_3–N was desorbed, respectively. Scanning electron microscopy (SEM) revealed that the dry–wet or freeze–thaw cycles did not alter the physical integrity of these resins. Freeze–thaw cycles had no effects on N and P adsorption or desorption characteristics of resins of the specific resins used in this study. Ion exchange resins used for in situ nutrient monitoring should be screened using similar techniques to assess its adsorption and desorption stability and physical integrity to fluctuating environmental conditions. Resin types and stability should be mentioned when comparisons are made to other studies.

Solid phase ion exchange resins are used to extract plant-available nutrients in situ and/or in the laboratory as a possible substitute for liquid extraction (Skogley and Dobermann, 1996; Giblin et al., 1994; Yang et al., 1991). Ion exchange resins are also widely used to measure nutrient movement or fluxes in agricultural fields (Zou et al., 1992; Sakadevan et al., 1994; Lehmann et al., 2001). In most soil studies, resins are used as a nutrient sink rather than a source to monitor seasonal fluctuations in nutrient status over the growing season.

Resin offers the advantage of representing the actual soil environmental conditions (i.e., temperature and moisture) and minimizes the need and cost of periodic soil sampling throughout the growing season. Under field conditions, resins have been used in the soil for periods ranging from 4 (Eghball, 2000) to 48 wk (Giblin et al., 1994). In the field, resins are exposed to a variety of changing physical conditions including freeze–thaw or dry–wet cycles. Kjonaas (1999) found that drying reduced adsorption of NO_3–N and NH_4–N by anionic and cationic resins, respectively. Kjonaas (1999) also observed no detectable effect of freezing on resin stability. Lehmann et al. (2001) have observed that the amount of NO_3–N and NH_4–N removal from solution was specific to resin type.

Studies have also shown minimal effect of storage conditions on recovery of ions adsorbed on resin (Skogley et al., 1997; Kjonaas, 1999). However, knowledge of the stability of resins under changing physical environments for in situ measurements of nutrient mineralization year-round in regions with soil freezing and fluctuating soil moisture is not well documented. The hypothesis of this experiment was that cycles of alternating freeze–thaw or dry–wet may not shift resin ion-adsorption/desorption characteristics or alter its effectiveness as a nutrient trap. For example, as the resin experiences dry–wet cycles in the summer, its efficacy as a nutrient sink should not be reduced or nutrients that had been previously trapped should not be released during the dry–wet cycles. The objective of this experiment was to measure changes in N and P adsorption and desorption of mixed bed resins that have undergone several freeze–thaw or dry–wet cycles.

MATERIALS AND METHODS

Resin Characteristics and Preparation

Anionic and cationic resins, strong base anion A464-D and strong acid cation C-249 (US Filter, Warrendale, PA) were used in the experiment. These resins were selected because they are currently being used to detect seasonal N mineralization in plots treated with manure (Eghball, 2000). Both anion and cation resins had a styrene-divinyl benzene matrix with an exchange capacity of 1.2 and 1.9 mol_c kg^{-1}, respectively (Table 1).

Water holding characteristic, size distributions, and ionic impurities of fresh (as received from manufacturer) and fresh mixed resins are listed in Table 1. The fresh mixed bed resin was prepared using a 1:1 oven-dry mass ratio of each resin type to facilitate anionic and cationic exchange. Subsamples of each resin type were placed in a forced air oven at 105 (±3)°C overnight to obtain moisture content. For consistency, drying at 105 (±3)°C is called oven-drying and the moisture status is described as oven-dry. Resin mix was presaturated with water and placed on a tempe cell (Soil Moisture Corp., Santa Barbara, CA) and subjected to 0.033 MPa to determine its moisture content (equilibration time of 3 to 4 d). Equilibrium was assumed when the daily outflow volume reached about 10% of the total outflow volume since initiating the pressure. Moisture content was determined by oven-drying overnight. Fresh mixed resin impurities for NH_4, NO_3, and PO_4 ions were determined after extraction with 2 *M* HCL (Dobermann et al., 1997).

M. Mamo, D. Ginting, and R. Renken, Dep. of Agronomy and Horticulture, Univ. of Nebraska, Lincoln, NE 68583; B. Eghball, USDA-ARS, Lincoln, NE 68583. A contribution of the University of Nebraska Agricultural Research Division, Lincoln, NE 68583. Journal Series No. 14151. Received 14 Feb. 2003. *Corresponding Author (mmamo3@unl.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: SEM, scanning electron microscope.

Table 1. Characteristics of ion resins.

Resin type	Matrix	Particle-size distribution, %				Capacity	Impurities‡			Water content§		
		>1000	1000–500	500–250	250–100		NH_4–N	NO_3–N	PO_4–P	Fresh	0.033 MPa	"Dry"
		μm				$mol_c\ kg^{-1}$	mM kg^{-1}			g kg^{-1}		
Strong base anion A464-D	styrene-divinyl benzene	0	77.6	22.5	0.2	1.2				553		
Strong acid cation C-249	styrene-divinyl benzene	0.3	72.5	27.1	0.3	1.9				465		
1:1 Mixed resin†							92.0	13.0	45.0	509	530	290–380

† 1:1 oven-dry mass ratio of each resin type combined to facilitate anionic and cationic exchange.
‡ Mixed resin impurities were determined by three consecutive 20 min extractions using 2 *M* HCl (Dobermann et al., 1997).
§ Water content achieved by oven-drying resin at 105(±3)°C overnight.
¶ Actual water content of resin achieved at the end of the dry cycle reported on oven-dry basis.

Adsorption Characteristic of Mixed Resins

Treatment of Mixed Resins with Freeze–Thaw or Dry–Wet Cycles

The mixed resin was exposed to 0, 1, and 30 freeze–thaw cycles. For each freeze-thaw cycle, a sealed container of mixed resin in triplicate was placed in a freezer at −20 (±3)°C for 16 h then thawed for 8 h at 21(±3)°C. Upon completion of a given freeze–thaw treatment cycle, the resin was stored at 7 (±3)°C until the adsorption isotherm experiments.

The dry–wet treatment also consisted of 0, 1, and 30 dry–wet cycles. The term *wet* in this experiment represents resin at fresh water content (509 g kg^{-1} oven-dry resin). The *dry* resin was achieved by air-drying resin in open containers placed in a forced air oven at 25 (±3)°C for 28 h (oven-dry moisture ranges from 290 to 380 g kg^{-1}). Drying was done at 25 (±3)°C to minimize resin shrinkage and irreversible chemical change before initiating the adsorption isotherm experiment on the resin. Dry condition was assumed when the oven-dry water content reached 55 to 70% of the water content at field capacity. These levels of drying were considered to be realistic especially for the widespread irrigated field conditions found in Nebraska. Under these field conditions, irrigation will be triggered when the water content reaches 60 to 70% of the water content at field capacity; however, we expect lower water content under dryland field conditions. We do not expect the resin to desiccate because even at 1.5 MPa (wilting point), the soil is near 99% relative humidity (Hanks and Ashcroft, 1980).

For the wetting cycle, the amount of water lost to reach the dry cycle was calculated and de-ionized water was added to the containers to bring the water content to the original fresh resin water content. The container was sealed and the resin and water left to equilibrate for 20 h before the next cycle. Upon completion of the final dry-wet cycle, de-ionized water was added to the starting moisture content and the resin was stored at 7 (±3)°C until the adsorption isotherm experiments.

Adsorption Isotherm of Treated Mixed Resin

The adsorption solution ion concentrations were selected based on soil measurements in field experiments that used the same mixed bed resins (Eghball, 2000). Two solutions were prepared, one containing NH_4–N and NO_3–N at 3.2 m*M* L^{-1} and the other containing PO_4–P at 0.97 m*M* L^{-1}. The solution to resin ratio needed for the adsorption experiment was established by preliminary experiments where resins were mixed with 3.2 m*M* L^{-1} NH_4–N, 3.2 m*M* L^{-1} NO_3–N, or 0.97 m*M* L^{-1} PO_4–P solutions for 24 h by varying resin mass with constant solution volume. Equilibrium solutions from each ratio (volume/oven-dry mass), 5:1, 10:1, 25:1, 70:1, 240:1, 600:1, 800:1, and 1200:1 were analyzed for NH_4–N and NO_3–N or PO_4–P. The 800:1 solution/resin ratio (volume/oven-dry mass) was selected for the NH_4–N and NO_3–N adsorption and a 600:1 ratio (volume/oven-dry mass) was selected for the PO_4–P adsorption. The ratio selection is based on ion adsorption >10 and <90% to ensure accurate and precise measurement of ion in solution and quantification of adsorption.

The mixed resins previously treated with cycles of freeze–thaw or dry–wet were equilibrated with solutions containing the N or P ions for periods of 1 h. The 1-h adsorption period was selected because testing of equilibrium periods (1, 24, 48, and 72 h) showed that equilibration was reached after 1 h (data not presented). The N adsorption was achieved by mixing 0.239 g of mixed resin (oven-dry basis at 105°C) with 200-mL of 3.2 m*M* L^{-1} N solution in 250-mL polyethylene bottles. The P adsorption was achieved by mixing 0.335 g (oven-dry) of mixed resin with 200-mL of 0.97 m*M* L^{-1} PO_4–P solution in 250-mL polyethylene bottles. The control mixed resin (not exposed to freeze–thaw or dry–wet cycles) was included simultaneously in the adsorption isotherm experiment. At the end of the adsorption period, the solution was decanted and analyzed for NH_4–N and NO_3–N using a Lachat (Zellweger Analytics, Milwaukee, WI) system and PO_4–P was analyzed using the molybdate blue method (Murphy and Riley, 1962).

Desorption Characteristics of Mixed Resins

Presaturation of Mixed Bed Resin with PO_4–P, NH_4–N, and NO_3–N

This experiment was conducted to determine if dry–wet or freeze–thaw cycles affected desorption of previously trapped resin N and P. In this case, the resins were subjected to different time lengths of freeze–thaw or dry–wet cycles after preloading resin with NO_3–N, NH_4–N, or PO_4–P. Sixty-five grams of fresh resin (32 g oven-dry equivalent) were saturated in 19 L of 0.97 P m*M* L^{-1} solution (as KH_2PO_4) or 25 L of 3.2 m*M* N L^{-1} (as NH_4NO_3) for 48 h at solution/resin ratios of 600:1 and 800:1, respectively. The 48-h equilibrium was used for ion saturation of resin with N and P since there was agitation to allow for fast equilibrium. After saturation, excess solutions were decanted and any entrained salt solution removed by placing the ion saturated resin on a filter paper covered funnel and rinsing it with 40 L of de-ionized water. The resin was air-dried to its original fresh water content by pouring it on an absorbent paper towel and monitoring its mass. To estimate the amount of P or N preloaded on the resin before the environmental cycles and subsequent desorption experiment, the resin was extracted by three consecutive 20 min extractions using 2 *M* HCl (Dobermann et al., 1997). The final total extractant volume and the mass of saturated resin used were 600:1 for PO_4–P and 800:1 for NO_3–N and NH_4–N. The extract was neutralized to near neutral pH with NaOH

and analyzed for PO_4–P or NH_4–N and NO_3–N. The extractable amount of PO_4–P, NH_4–N, and NO_3–N preloaded on the resin was 245, 655, and 1070 m*M* kg^{-1}, respectively. Freeze–thaw or dry–wet treatments were applied on the resins preloaded with N or P in cycles of 0, 1, and 30 as described above. At the end of the treatment cycles, 0.835 g oven-dry equivalent weight resin was extracted with 20 mL of de-ionized water for 1 h. The solution was separated from the resin to measure desorbed PO_4–P or NH_4–N and NO_3–N.

Resin Physical Integrity

Preliminary observation during determination of resin water-holding properties indicated that fresh resin expanded during saturation and shrunk during drying. To evaluate swelling of fresh resin, 13 to 15 g of fresh resin were placed into a 50-mL graduated-flask; 25 mL distilled water was added, and the total volume was immediately recorded. The initial volume of fresh resin was determined by the difference between the total volume minus 25 mL. The resin was left in the flask for 24 to 48 h to allow for saturation. After saturation, the water was decanted carefully from the flask (not to loose any resin grains), and the excess was removed from the resin by drying with a paper towel. Immediately, the volume of saturated resin was determined with the same procedure of determining the volume of fresh resin. The swelling was expressed (in percentage) as the ratio of the difference of volume between saturated minus fresh resin and the volume of fresh resin.

Scanning electron microscopy was performed on fresh resin and resin treated with 10 dry–wet or freeze–thaw cycles. Six to eight resin samples were attached with carbon adhesive tabs onto stubs and coated with 20- to 30-nm thick gold/palladium in a Hummer II (Anatech Ltd., Union City, CA) or an Emitech K575X (Emitech Products Inc., Houston, TX) sputtering unit. Specimens were examined and digitized with a Hitachi 3000N (Hitachi, Japan) SEM operated at 15 kV. It was observed that the Hummer II sputtering unit cracked the surface of the resin and therefore images prepared with the Emitech K575X unit are presented.

Data Analysis

The experimental design was a randomized complete block (RCB) with three replications. Freeze–thaw or dry–wet cycle effects on resin N and P adsorption or desorption were compared with the untreated (check) resin using a GLM model on SAS version 8 (Statistical Analysis Software, Statistical Analysis System, 1999). Mean separation was done using the Duncan–Waller test within each nutrient. Significance level was set at a probability of 5%.

RESULTS AND DISCUSSION

Moisture Condition of Resin

Fresh resin water content was 509 (g kg^{-1}), which was slightly drier than the water content at 0.033 MPa (Table 1). The majority of resin water was interstitial, that is, within the resin granule rather than between the granules. The significant proportion of interstitial water explained why it took a long drying time (28 h) to deplete 25 to 43% of the fresh resin water content. As will be discussed in a later section, the interstitial water property was very important in controlling both shrinking and swelling and desorption of ions as the resins underwent drying and wetting.

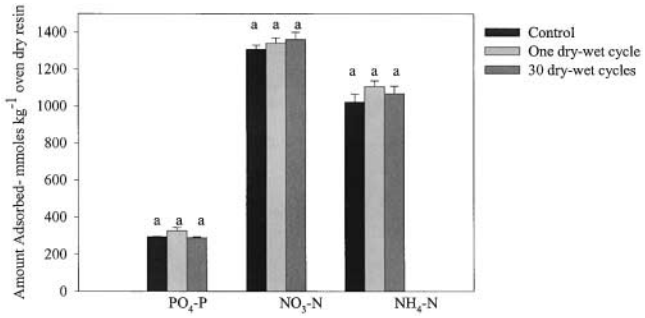

Fig. 1. Effect of dry–wet cycles on ion exchange resin adsorption of PO_4–P, NO_3–N, and NH_4–N. Bars with the same letter for each ion are not significantly different at $P < 0.05$.

Adsorption of Nitrogen and Phosphorus on Ion Exchange Resins

Freeze–Thaw and Dry–Wet Cycles

The concentration of NO_3–N (3.2 m*M*) mixed with the resin was three times higher than the PO_4–P (0.97 m*M* L^{-1}), thus, NO_3–N adsorption by resin was four to five times more than PO_4–P under both dry–wet and freeze–thaw cycles (Fig. 1 and 2). Under field conditions, more NO_3–N is found in soil solution compared with PO_4–P; therefore, NO_3–N recovery by resin is expected to be higher than PO_4–P. Although a 1:1 ratio was used to make the mixed bed resins and the concentration of NO_3–N and NH_4–N added were similar; there was less NH_4–N than NO_3–N adsorbed. The lower NH_4–N adsorption in comparison with NO_3–N is not well understood. Perhaps higher resin impurities of NH_4–N (92 m*M* kg^{-1}) compared with NO_3–N (3 m*M* kg^{-1}) may have contributed to the differences.

Neither the freeze–thaw nor the dry–wet cycles changed the resin adsorption characteristics for N and P compared with the control (Fig. 1 and 2). Kjonaas (1999) also observed no effect of freezing and thawing on resin stability or N adsorption efficiency when resin was exposed to freezing temperature before extraction. Kjonaas (1999) also observed reduced adsorption of NO_3–N when resins were air-dried for 48 h before N addition. Similarly, Lehmann et al. (2001) using mixed bed resin (Amberlite MB 6 Na^+/Cl^-), observed a decrease in NO_3–N and NH_4–N adsorption/absorption after five repeated drying exposures, while no effect was observed for another mixed bed resin (Amberlite MB 20 Na^+/Cl^-). As demonstrated by Lehmann et al. (2001),

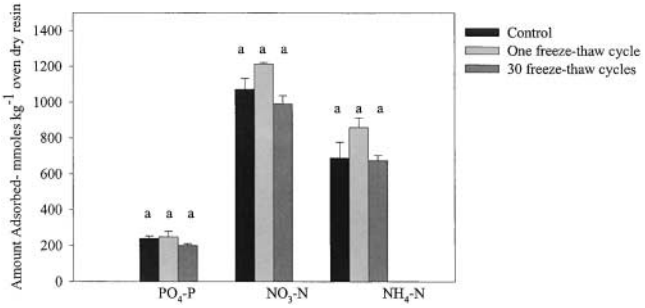

Fig. 2. Effect of freeze–thaw cycles on ion exchange resin adsorption of PO_4–P, NO_3–N, and NH_4–N. Bars with the same letter for each ion are not significantly different at $P < 0.05$.

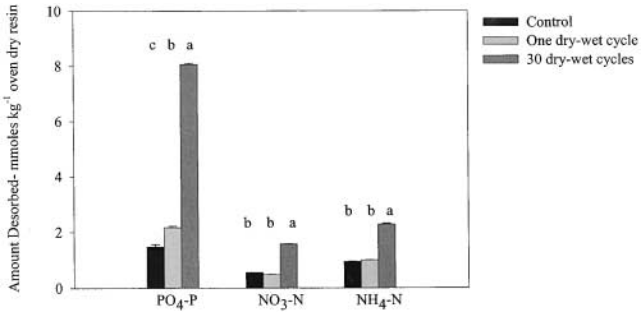

Fig. 3. Effect of dry–wet cycles on ion exchange resin desorption of PO_4–P, NO_3–N, and NH_4–N. Bars with the same letter for each ion are not significantly different at $P < 0.05$.

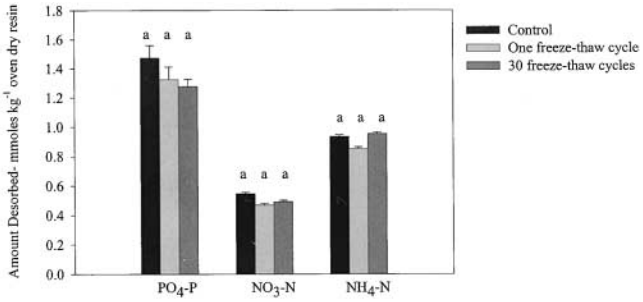

Fig. 4. Effect of freeze–thaw cycles on ion exchange resin desorption of PO_4–P, NO_3–N, and NH_4–N. Bars with the same letter for each ion are not significantly different at $P < 0.05$.

different resin types will respond differently to similar environmental conditions.

Desorption of Phosphorus and Nitrogen from Ion Exchange Resins

Dry–Wet Cycles

The amount of PO_4–P desorbed increased as the dry–wet cycle increased (Fig. 3). The amount of NO_3–N and NH_4–N desorbed increased only at the highest (30) dry–wet cycle. Under each dry–wet cycle (Fig. 3), PO_4–P desorption was higher than that of NO_3–N. This may be due to higher affinity of resin toward NO_3–N than PO_4–P. Compared with NO_3–N, the increase in PO_4–P desorption was much higher with increasing dry–wet cycles. The PO_4–P desorbed were 2.7, 4.5, and 5.1 times of NO_3–N desorption at 0, 1, and 30 dry–wet cycles, respectively. There was also higher desorption of NH_4–N under the dry–wet cycles compared with NO_3–N.

The percentage of PO_4–P, NH_4–N, and NO_3–N desorbed at the highest dry-wet cycle was 3.3, 0.35, and 0.15, respectively. Giblin et al. (1994) reported significant desorption of NO_3–N (as large as 80%) and PO_4–P in anion exchange resins preloaded with N and P in arctic soils for 2 to 44 wk. However, they attributed the desorption to high HCO_3 levels rather than environmental conditions. The difference observed in the percentage of ions desorbed between this study and that of Giblin et al. (1994) is indicative of variation in response to environmental conditions among resin types. The implication of this result is that under conditions when resins are buried in the field, occurrence of dry–wet cycles can desorb some of the previously adsorbed P and N and thereby underestimate the amount present in the soil. In addition, if resins are used to estimate mineralization of N and P, the environmental factor of dry–wet cycles can potentially contribute to erroneous estimation of the mineralized N and P levels (maximum of 3.3%). The amount of ions desorbed in our study

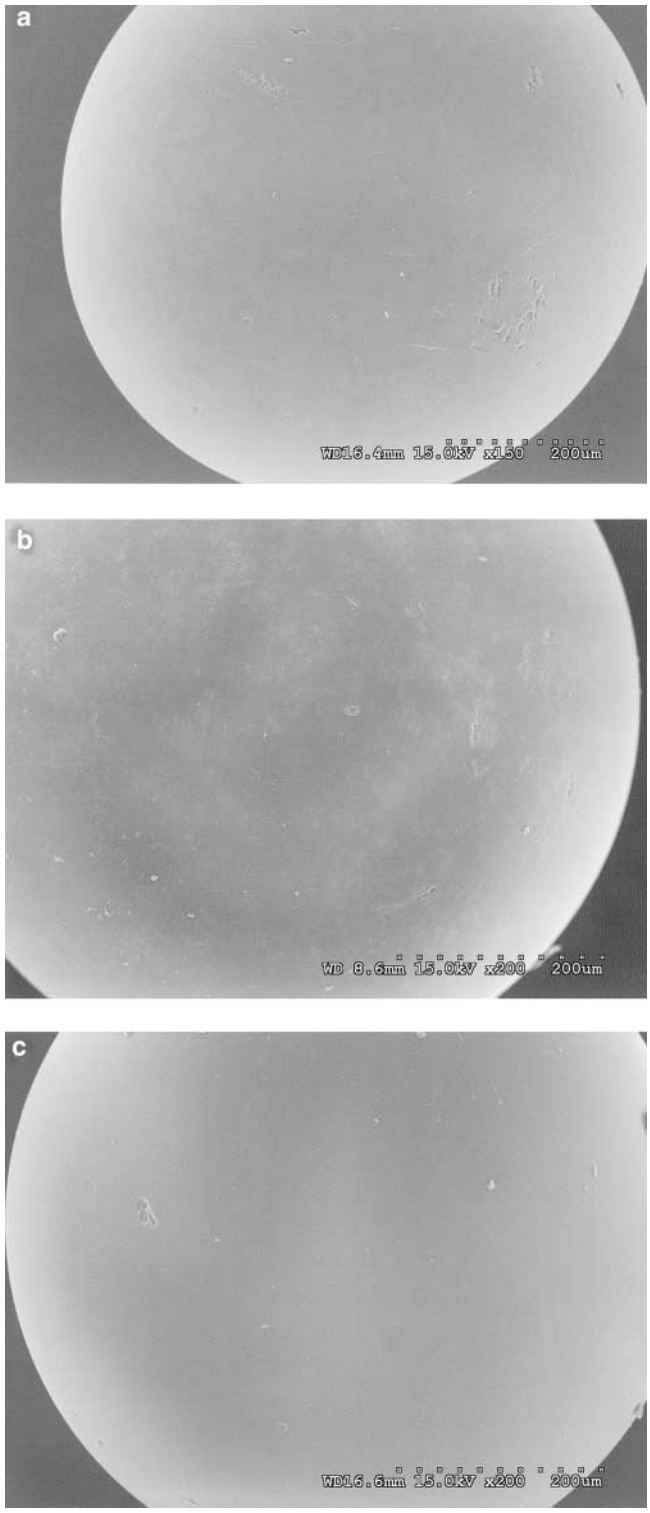

Fig. 5. Scanning electron microscopy of (a) fresh resin, (b) resin treated with dry-wet cycles, and (c) resin treated with freeze–thaw cycles.

may not be significant considering the errors associated with analytical measurements plus the degree of variation contributed by the nonhomogeneous nature of soil.

Freeze–Thaw Cycles

Unlike the dry–wet cycles, the freeze–thaw cycles did not significantly affect the desorption of PO_4–P, NO_3–N, or NH_4–N (Fig. 4). The swelling and shrinking mechanism of resins that resulted in expelling nutrient solution out of the interstitial sites during shrinking (from wet to dry or from frozen to thawed condition) may have been greater during the dry–wet cycles compared with the freeze–thaw cycles. This was confirmed by the expansion of fresh resin after saturation with distilled water. The average expansion of resin volume was 18.8% (ranged from 13.3–23.2%). The influence of resin shrink–swell upon dry–wet cycles and the subsequent ion desorption implied that the integrity of the resin may be affected. The physical integrity of resin surfaces was then observed with SEM.

Physical Integrity of Resin

As shown in Fig. 5, the resin did not show changes on the surface due to dry–wet or freeze–thaw treatments. This confirms the results of the adsorption and desorption that environmental conditions did not physically alter the surfaces of these specific types of ion exchange resin. Therefore, shrinking was the main process causing increased desorption of PO_4–P, NO_3–N, and NH_4–N after dry–wet cycles.

It also appears that the dry conditions in the wet–dry cycle of this study was not extreme because in a preliminary trial with SEM, extreme drying conditions to coat the resin with gold/palladium using the Hummer II produced deep cracks on the resins (figure not presented). The specific conditions of the Hummer II that generated heat and resulted in deep cracks and extreme drying included sputtering for 2 min with current of 10 mA under a vacuum pressure of 1.3×10^{-5} to 1.9×10^{-5} MPa.

CONCLUSIONS

For the resin used in this study, adsorption of N and P was not changed after resins had undergone several dry–wet or freeze–thaw cycles. Freeze–thaw cycles did not induce desorption of ions from resin, however, dry–wet cycles induced desorption of N and P (<3.3% of total) associated with shrinking of resins. The extent of desorption after a prolonged dry–wet cycle was not due to disintegration of resin structure. While ion exchange resins are good tools to employ in the field for in situ short- or long-term monitoring of nutrients, the specific resin type should be screened using similar techniques to assess its adsorption and desorption stability and physical integrity to fluctuating environmental conditions before deployment.

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